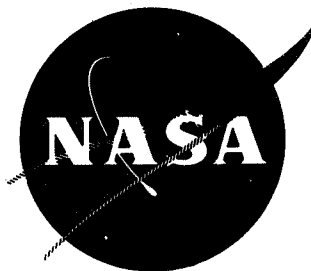


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SRI Project PMD 7359



THE RELATIONSHIP OF OXIDE SCALE DISPLACEMENT REACTIONS TO THE
OXIDATION BEHAVIOR OF IN-100

by

D. L. Douglass

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NASA Lewis Research Center

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TOPICAL REPORT

THE RELATIONSHIP OF OXIDE SCALE DISPLACEMENT REACTIONS TO THE
OXIDATION BEHAVIOR OF IN-100

by

D. L. Douglass

STANFORD RESEARCH INSTITUTE

Menlo Park, California 94025

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May 1969

CONTRACT NAS 3-11165

NASA Lewis Research Center
Cleveland, Ohio

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Carl E. Lowell, Research Advisor

Materials and Structures Division

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ABSTRACT

Attempts to induce oxide displacement reactions by inert annealing of preoxidized samples were unsuccessful due to the formation of Al_2O_3 and NiTiO_3 . These compounds formed in lieu of NiO which existed to only a minor extent. Subsequent oxidation of pretreated samples at either 1000 or 1100°C showed a gross difference in oxide morphology. Internal oxidation and deep penetration of the oxide into the alloy occurred at 1000°C, whereas no internal oxidation occurred at 1100°C. Improvement of oxidation resistance is discussed in terms of high-temperature prefilming at 1100°C instead of by the originally proposed displacement reactions.

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ACKNOWLEDGEMENT

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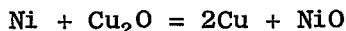
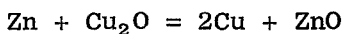
SUMMARY

IN-100 was subjected to a series of pretreatments prior to oxidation at either 1000 or 1100°C. The initial step was preoxidation for various times at 800°C, which generally resulted in the formation of thin films consisting mainly of Al_2O_3 and NiTiO_3 , although it had previously been reported that these films were primarily NiO .¹ Inert anneals were performed at either 1000 or 1100°C for various times, ostensibly to enable displacement reactions to occur such that the more reactive component Cr would reduce the base metal oxide NiO to form Cr_2O_3 . Although displacement reactions did not take place, there were some significant structural and morphological changes in the oxides scales, which formed during subsequent oxidation at 1000 and 1100°C, that could be attributed to the inert anneals. Internal oxidation occurred at 1000°C, forming a zone of Al_2O_3 particles, whereas oxidation at 1100°C resulted in continuous films, which were more protective than the scales containing the zone of internally oxidized particles. This effect was attributable to the inert anneals, for similar oxidation tests¹ without any pretreatments resulted in extensive internal oxidation at both oxidation temperatures.

Extensive spalling of the films occurred during oxidation at both 1000 and 1100°C. If this problem could be solved, pretreatments might offer a means of reducing the oxidation rate of IN-100.

INTRODUCTION

Some dilute binary alloys containing a more oxidizable element as the alloying addition form the oxide of the more noble metal first and subsequently that of the less noble metal. The time required to form the second oxide depends on many factors, but in many cases it forms by internal oxidation. Another generalization is that the second oxide is more protective than the oxide of the more noble metal. It would then follow that any process that allowed the less noble metal oxide to form quickly would offer a means for increasing the oxidation resistance of the alloy. This corollary has been predicted^{2,3} although not studied extensively. Levin and Wagner⁴ found a marked reduction in the parabolic rate constants for alpha brasses as well as for an alloy of 62Cu-38Ni as a result of inert isothermal anneals after an initial oxidation period. Metallographic sections of the oxides definitely established that the following displacement reactions occurred in Cu-Zn and in Cu-Ni, respectively:



An alloy of 85Cu-15Zn exhibited a 14-fold reduction in the oxidation rate of 700°C after a 1-hour inert isothermal anneal.

Nickel-base and cobalt-base alloys almost always contain chromium additions (as well as numerous other elements) and form Cr_2O_3 as a major constituent of the protective oxide film. As in the case of copper-base alloys, binary alloys of Ni-Cr and Co-Cr also form the base metal oxides initially, even though nickel and cobalt are considerably less active toward oxygen than is chromium. It would thus appear that both systems should be analogous to the Cu-Zn and the Cu-Ni systems in that a displacement reaction in the oxide film would enable Cr_2O_3 to form sooner with a resultant decrease in the oxidation rate.

Superalloys such as IN-100 contain approximately 4 to 5% of both aluminum and titanium in addition to the chromium. Both of these elements are very strong oxide formers, even more so than chromium, and would be expected to reduce during inert annealing any NiO or CoO that formed initially on nickel and cobalt base alloys, respectively. It had been reported that IN-100 acted somewhat like Ni-10Cr during the initial stages of oxidation in that NiO was the first oxide to form.¹ Based on this observation and the results of Levin and Wagner, it was hoped that suitable inert anneals would allow displacement reactions to occur in the scales of this alloy and thereby reduce the oxidation rate.

EXPERIMENTAL PROCEDURES

Investment-cast samples of IN-100 were obtained from the Misco Division of Howmet Corp. in the form of bars 1 in. x 8 in. x $\frac{1}{8}$ in., having a composition of

| | | | | | |
|----|--------|----|-------|----|---------|
| Cr | 10.25% | Ti | 4.68% | Mn | <0.1 |
| Co | 15.15 | V | 0.79 | Fe | 0.07 |
| Mo | 3.20 | C | 0.18 | B | 0.012 |
| Al | 5.52 | Si | <0.1 | Ni | Balance |

Samples for oxidation were cut from the bars and electropolished in a solution of 60% H_3PO_4 - 40% H_2SO_4 containing 10 g CrO_3 /liter. All samples were then preoxidized for either two or seven days at 800°C. The preoxidized samples were encapsulated in vacuum in Vycor tubes and subjected to inert anneals at either 1000 or 1100°C. Oxidation was performed in a Cahn recording microbalance which was previously described.⁵ Various X-ray diffraction metallographic, and electron microprobe analyses were performed after oxidation on selected samples.

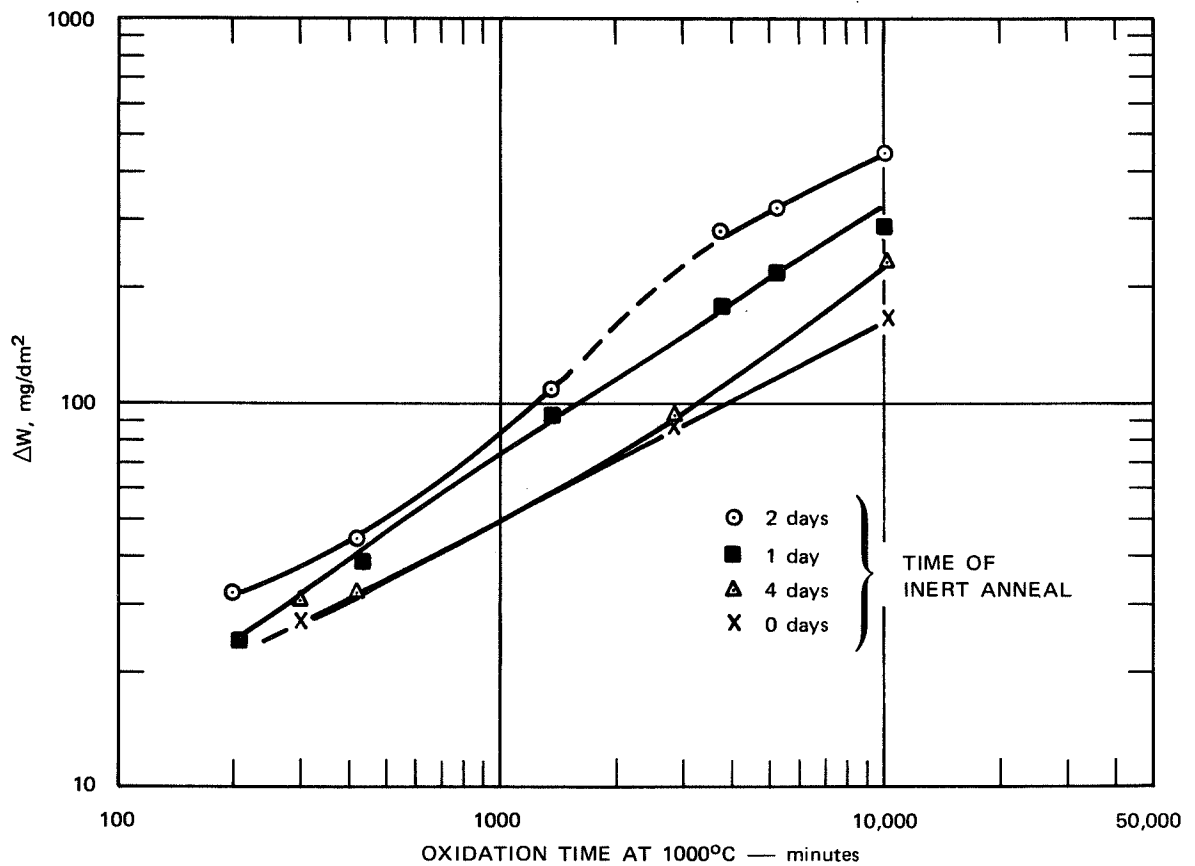
RESULTS

Treatments were designed so that the following sequences could be studied:

| <u>Preoxidation(^oC)</u> | <u>Inert Anneals(^oC)</u> | <u>Oxidation(^oC)</u> |
|------------------------------------|-------------------------------------|---------------------------------|
| 2 days 800 | 1000 | 1000 |
| 2 days 800 | 1000 | 1100 |
| 2 days 800 | 1100 | 1000 |
| 2 days 800 | 1100 | 1100 |
| 7 days 800 | 1000 | 1000 |
| 7 days 800 | 1000 | 1100 |
| 7 days 800 | 1100 | 1000 |
| 7 days 800 | 1100 | 1100 |

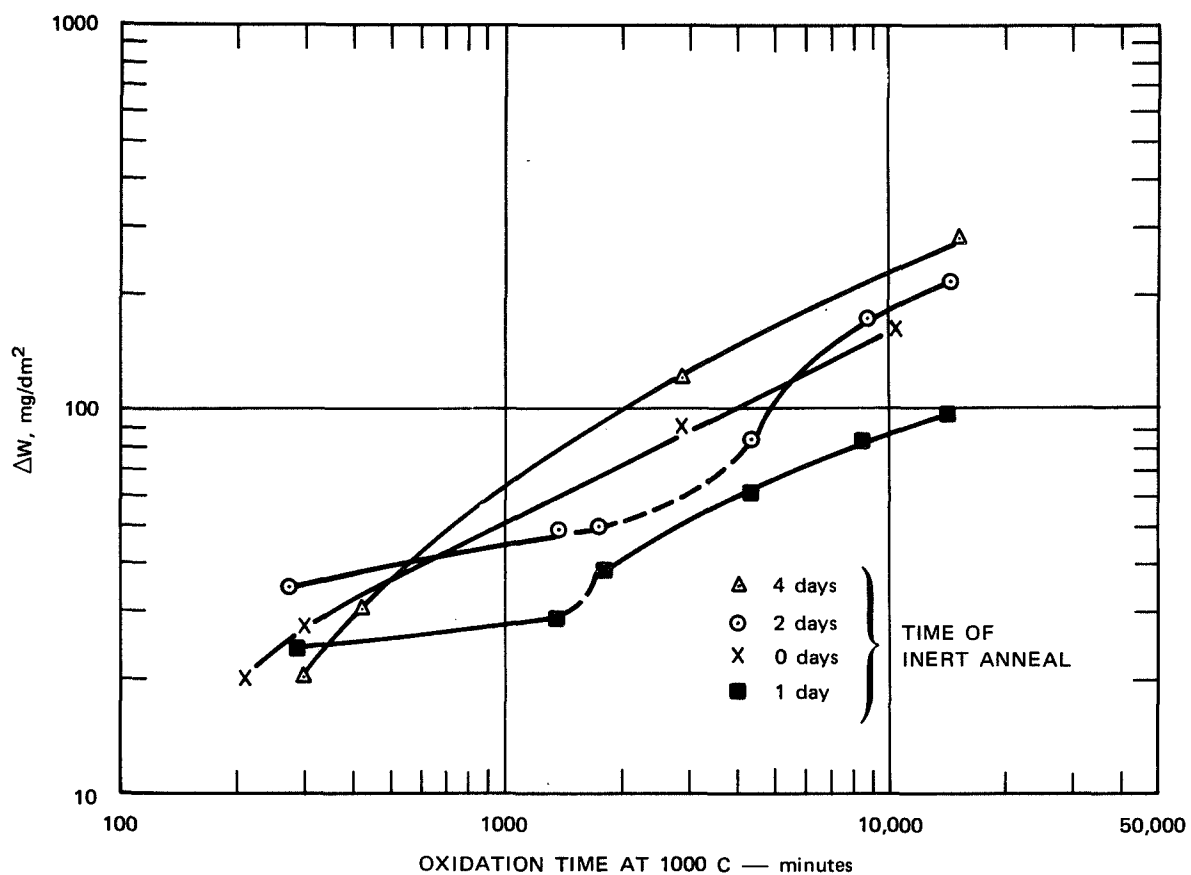
Data for kinetics of oxidation are shown for five of the treatments in Figs. 1-5. Samples that were subjected to the treatments for which data are not given exhibited too much spalling during oxidation to enable meaningful curves to be drawn. Further complications existed due to the lack of reproducibility in duplicate or triplicate samples. However, in spite of the difficulties, some trends were apparent.

For samples preoxidized 2 days at 800^oC, oxidation resistance at 1000^oC was improved slightly when the inert anneal was performed at 1100^oC rather than at 1000^oC. When all other conditions were constant, e.g., oxidation at 1000^oC after an inert anneal at 1000^oC; an increase in the preoxidation time from two to seven days had virtually no effect. However, the longer preoxidation time increased the oxidation rate for samples annealed at 1100^oC and oxidized at 1000^oC. In summary, for samples oxidized at 1000^oC, the time for the preoxidation and the temperature of the inert anneal had either little or a slightly deleterious effect on the oxidation resistance.



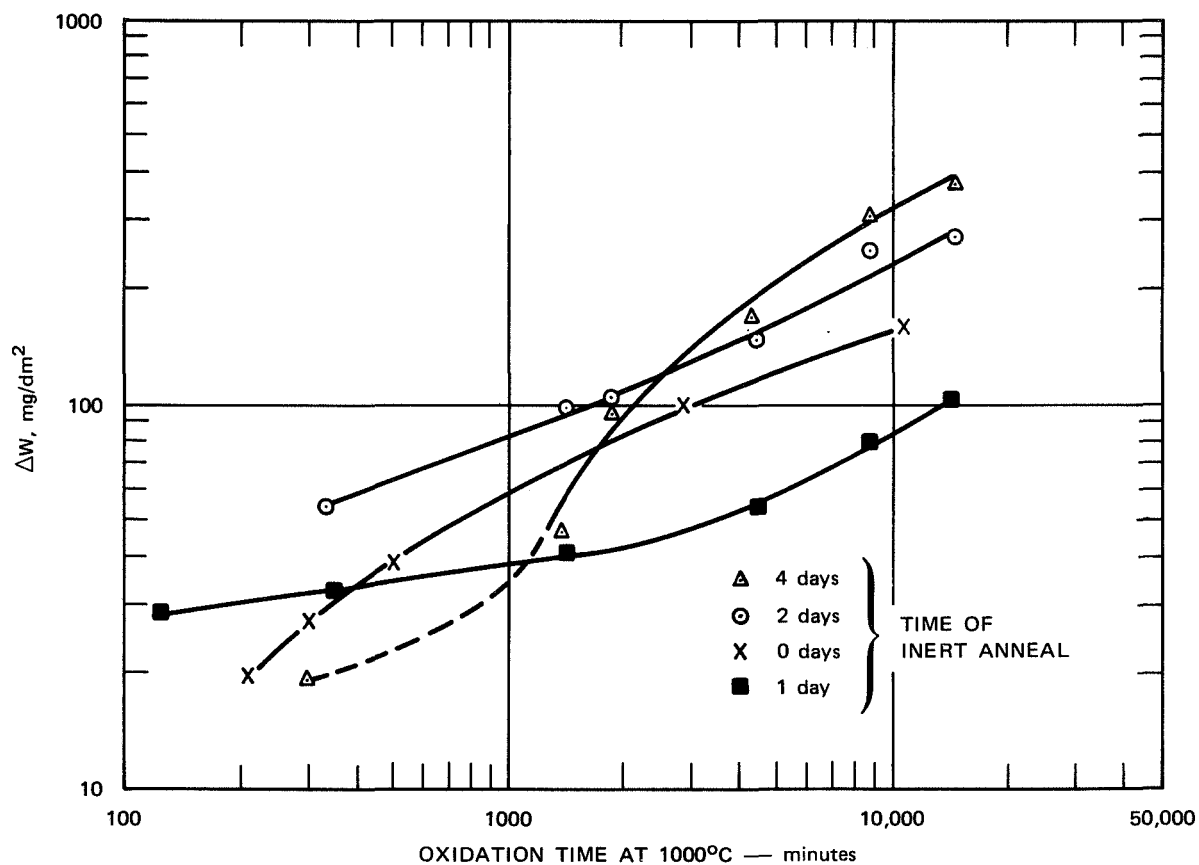
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FIGURE 1 IN-100; PREOXIDIZED 7 DAYS 800°C; INERT ANNEAL AT 1100°C FOR VARIOUS TIMES; OXIDIZED AT 1000°C



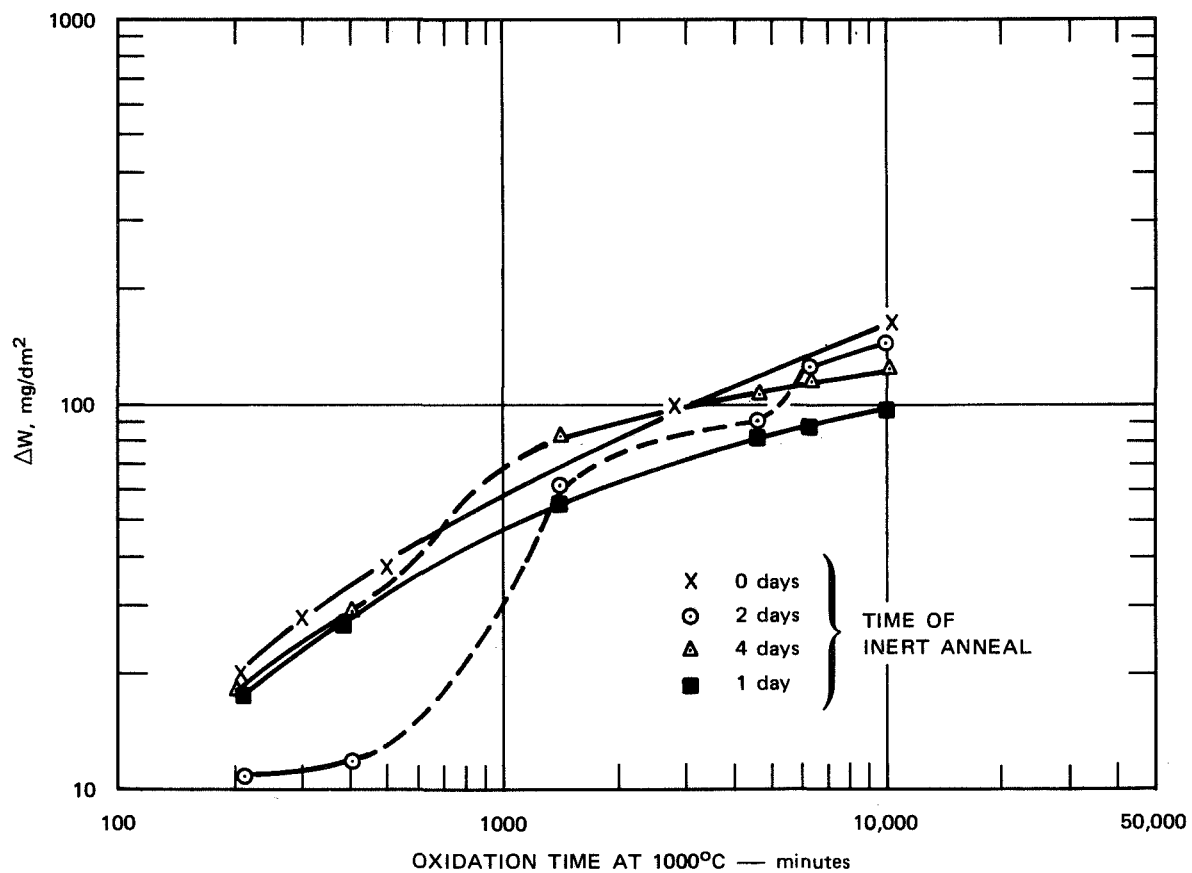
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FIGURE 2 IN-100; PREOXIDIZED 7 DAYS 800°C; INERT ANNEAL AT 1000°C FOR VARIOUS TIMES; OXIDIZED AT 1000°C



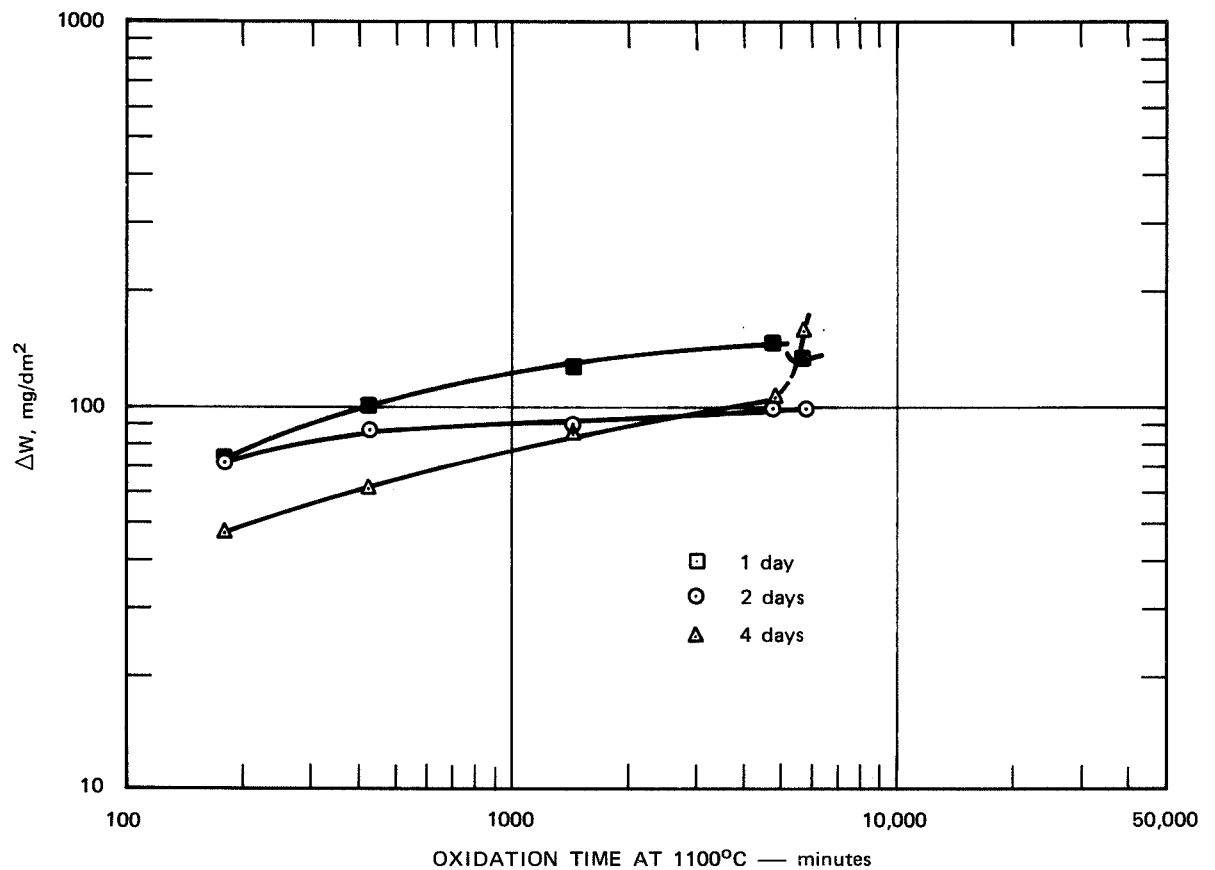
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FIGURE 3 IN-100; PREOXIDIZED 2 DAYS 800°C; INERT ANNEAL AT 1000°C FOR VARIOUS TIMES; OXIDIZED AT 1000°C



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FIGURE 4 IN-100; PREOXIDIZED 2 DAYS 800°C; INERT ANNEAL AT 1100°C FOR VARIOUS TIMES; OXIDIZED AT 1000°C



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FIGURE 5 IN-100; PREOXIDIZED 7 DAYS 800°C; INERT ANNEAL AT 1000°C FOR VARIOUS TIMES; OXIDIZED AT 1100°C

Oxidation tests performed at 1100°C were meaningless on all but one batch of samples due to excessive spalling. Apparently the thicker films formed at this temperature were more highly stressed than those at 1000°C, and the stresses were more than sufficient to rupture and spall the films. It is interesting to note, however, that the weight gains at the longest time tested during oxidation at 1100°C were much lower than those associated with samples oxidized at 1000°C, although the initial weight gains were higher at 1100°C. In other words, a definite leveling out in the weight-gain-time curve was occurring. It appears, therefore, that if the spalling problem could be resolved, inert anneals might have a favorable effect at 1100°C.

X-Ray Diffraction

To strip oxidation films from the samples, the oxides were scored and the coated samples exposed to a solution of bromine (10%)-ethyl acetate at 75°C. The metal was dissolved away from under the films which floated free and were collected, cleaned, and subjected to diffraction analysis. The relative intensities of the various phases existing in the oxide scales after the displacement reactions are summarized in Table I.

Structure of Oxide Scales

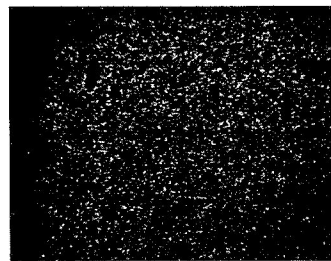
Some representative micrographs and X-ray images of scales formed during oxidation at 1000 and 1100°C after various pretreatments are shown in Figs. 6-10. An appreciable difference exists between scales formed by oxidation at 1000°C and those formed by oxidation at 1100°C regardless of the pretreatment. Internal oxidation occurred at the lower temperature resulting in discrete particles of an aluminum-rich oxide, most likely Al_2O_3 , whereas at 1100°C internal oxidation did not occur. Oxidation was heterogeneous at 1000°C inasmuch as some areas on a given sample did not exhibit internal oxidation, e.g.,

Table I

X-RAY DIFFRACTION ANALYSES OF STRIPPED OXIDATION FILMS

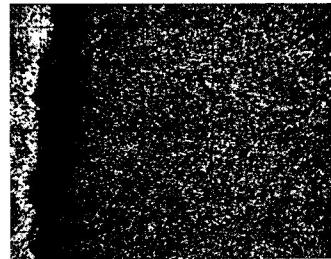
| Sample History | Relative Intensity of Various Oxides* | | | | | |
|--|---------------------------------------|-----|--------|--------------------|--------------------------------|-----------------------------------|
| | Al ₂ O ₃ | NiO | Spinel | NiTiO ₃ | Cr ₂ O ₃ | Ni ₂ Ti ₄ O |
| Preoxidized 2 days 800°C | m | w | vw | s | - | - |
| Preoxidized 2 days 800°C + 1 day anneal 1000°C | w | s | m | w | m | - |
| Preoxidized 2 days 800°C + 1 day anneal 1100°C | s | w | w | m | - | m |
| Preoxidized 2 days 800°C + 2 day anneal 1100°C | s | w | w | m | - | m |
| Preoxidized 2 days 800°C + 4 day anneal 1100°C | s | w | - | m | - | m |
| Preoxidized 7 days 800°C + 1 day anneal 1000°C | s | m | vw | vw | - | w |
| Preoxidized 7 days 800°C + 4 day anneal 1000°C | s | m | - | vw | - | w |
| Preoxidized 7 days 800°C + 1 day anneal 1100°C | s | s | vw | - | - | m |
| Preoxidized 7 days 800°C + 2 day anneal 1100°C | s | s | - | w | - | s |

*s = strong, m = medium, w = weak, vw = very weak.

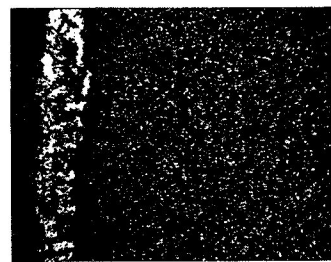


X-RAY IMAGES

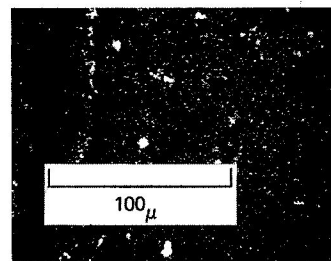
Ni-K_α



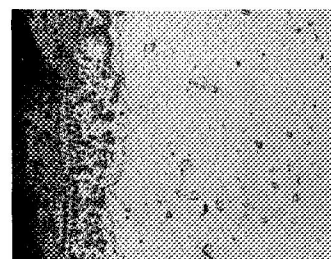
Cr-K_α



Al-K_α



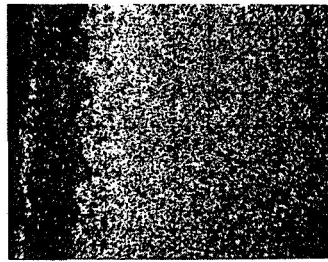
Ti-K_α



MICROGRAPH

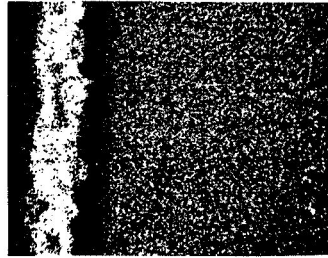
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FIGURE 6 STRUCTURE OF SCALE ON IN-100 PREOXIDIZED
2 DAYS AT 800°C AND OXIDIZED 7 DAYS AT 1000°C

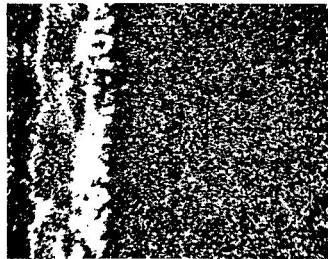


X-RAY IMAGES

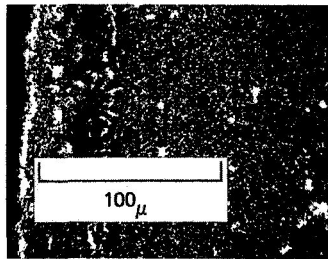
Ni-K_α



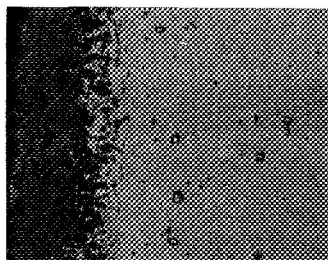
Cr-K_α



Al-K_α



Ti-K_α

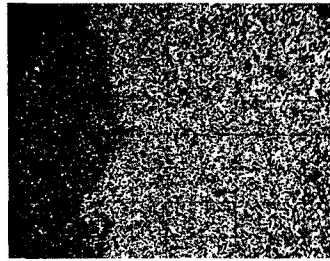


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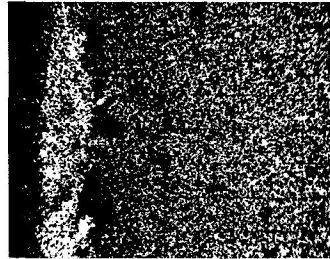
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FIGURE 7 STRUCTURE OF SCALE ON IN-100 PREOXIDIZED 7 DAYS AT 800°C, INERT-ANNEALED 4 DAYS AT 1000°C, AND OXIDIZED 7 DAYS AT 1000°C

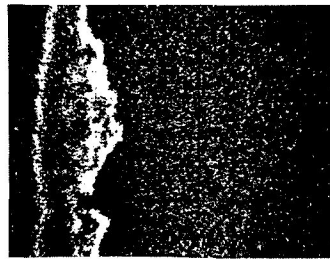
X-RAY IMAGES



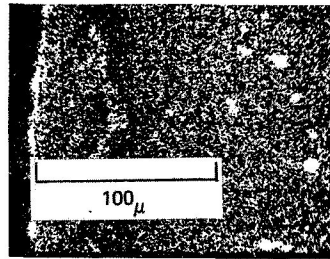
Ni-K $_{\alpha}$



Cr-K $_{\alpha}$



Al-K $_{\alpha}$



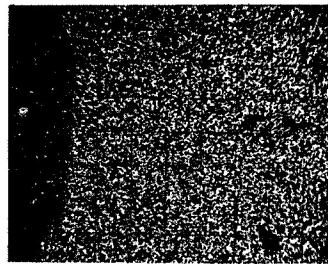
Ti-K $_{\alpha}$



MICROGRAPH

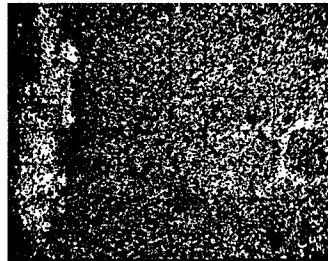
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FIGURE 8 STRUCTURE OF SCALE ON IN-100 PREOXIDIZED 7 DAYS AT 800°C, INERT-ANNEALED 4 DAYS AT 1100°C, AND OXIDIZED 7 DAYS AT 1000°C



X-RAY IMAGES

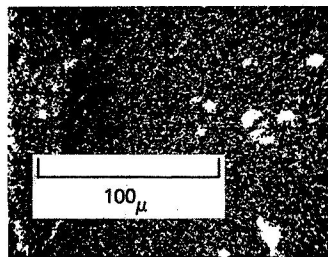
Ni-K_α



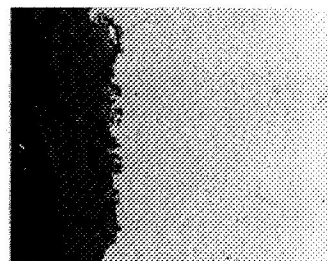
Cr-K_α



Al-K_α



Ti-K_α

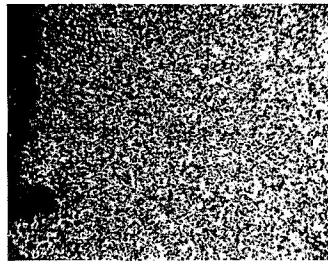


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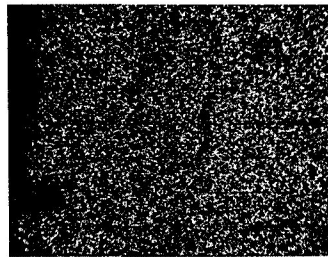
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FIGURE 9 STRUCTURE OF SCALE ON IN-100 PREOXIDIZED 7 DAYS AT 800°C, INERT-ANNEALED 4 DAYS AT 1100°C, AND OXIDIZED 4 DAYS AT 1100°C

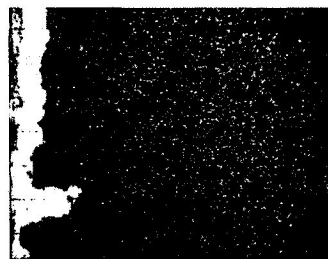
X-RAY IMAGES



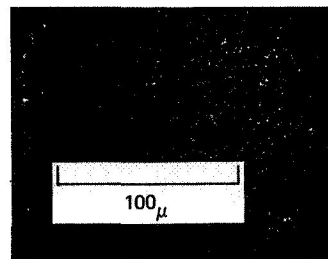
Ni-K_α



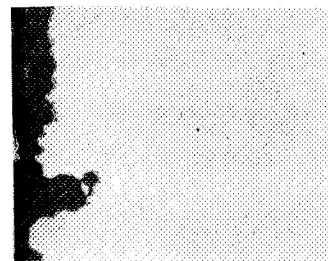
Cr-K_α



Al-K_α



Ti-K_α



MICROGRAPH

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FIGURE 10 STRUCTURE OF SCALE ON IN-100 PREOXIDIZED 7 DAYS AT 800°C, INERT-ANNEALED 2 DAYS AT 1000°C, AND OXIDIZED 7 DAYS AT 1100°C

Fig. 8. However, no internal oxidation whatsoever was observed when oxidation was performed at 1100°C, and the oxides formed at this temperature were thinner than those formed at 1000°C.

X-ray image micrographs showed a very low nickel content in the scales for all conditions of oxidation and pretreatment. The compact scales formed at 1000°C consisted of an outer titanium-rich phase, and aluminum-rich phase directly below the outermost oxide, a chromium-rich phase in the middle (constituting the major thickness of the scale), and an innermost aluminum-rich oxide. The scales overlying the portions that underwent internal oxidation consisted of a thin outer layer of nickel aluminate (?), a thin titanium-rich phase, a more massive layer of chromium oxide, and finally the aluminum oxide particles in the zone of internal oxidation.

In the absence of interrupted anneals, the main portion of the scale was chromium-rich oxide containing titanium. The internally oxidized zone containing aluminum oxide was below this layer. In all cases, significant chromium depletion occurred in the zone of internal oxidation. The intermetallic compound particles in the alloy itself were titanium-rich. All of the other elements scanned--chromium, aluminum, and nickel--appeared to be depleted in these particles.

Samples oxidized at 1100°C generally contained scales that were predominantly Al_2O_3 , with small isolated particles of a titanium-rich phase within the alumina, Fig. 9, or scales that were triplex in nature. The triplex scales were titanium-rich on the outside, chromium-rich in the center, and aluminum-rich at the oxide-metal interface. Each zone appeared to contain the other three elements. Nickel was noticeably absent in all zones of these scales.

DISCUSSION

The basis for the present study is that the first oxide to form is that of the base metal. Generally the base metal oxide is less protective than oxides formed by the alloying additions. In other words, the alloying additions are made to improve the oxidation resistance by any of several mechanisms, one of which is the formation of a completely different oxide. There is a certain time period required to form the new oxide if the total amount of solute is below some critical level (about 25-30% Cr in Ni-Cr alloys).

If some treatment can be performed so that the desired oxide will form faster than normally expected, a marked improvement in oxidation resistance can be achieved. Such a treatment is an inert anneal that permits a displacement reaction to occur as in the case of oxidation of Cu-Zn and Cu-Ni alloys.^{2,3} On the basis that NiO was the first and most significant oxide to form during the oxidation of IN-100,¹ it was logical to expect that displacement reactions might offer the possibility of reducing the oxidation rate of this alloy. Unfortunately, it was found that other oxides, notably Al_2O_3 , formed during the low temperature preoxidation treatment, and that the aforementioned observation of NiO forming as the initial oxide was wrong. Consequently, the discussion of displacement reactions per se for alloys in this system is not significant. On the other hand, it was found serendipitously that marked differences in oxide morphology existed, depending upon oxidation and preoxidation conditions. The main differences were those of internal oxidation versus no internal oxidation which can lead to significant differences in degradation of metals during oxidation. This subject will be the main point considered.

Internal Oxidation

As mentioned previously, the addition of an alloying element to improve oxidation resistance usually is performed with the expectation that this element will form a continuous film of its own oxide. The stable oxide so formed is presumed to have low diffusivities of both cations and anions, and thus a marked decrease in the oxidation rate is expected. However, the higher reactivity of the added elements with oxygen may under certain circumstances lead to internal oxidation of the solute, in which case no external film of this oxide forms. In essence the addition offers no protection, and the oxidation rate will remain high. A transition from internal oxidation to external oxide film formation occurs at a critical composition that is oxygen pressure and temperature dependent.⁶ The transition is marked by an abrupt decrease in the oxidation rate.

Two factors are particularly important with respect to the transition. First, the composition must exceed the critical value, and second, the dissolution of oxygen in the metal must be prevented. The first of these factors, e.g., the critical composition, is a function of both temperature and oxygen pressure, hence pretreatments at temperatures other than the oxidation temperature may provide the right conditions to form an external film.

Wasielowski¹ found internal oxidation at all temperatures studied, ranging from 1600°F (872°C) to 2000°F (1093°C). The thickness of the internally oxidized zone ranged from approximately 2 microns to about 50 microns for samples oxidized 100 hr at 1600 and 2000°F, respectively. These values are compared to those found in this study of 30 microns after 168 hr oxidation at 1000°C and zero microns after 168 hr oxidation at 1100°C. The lack of any pretreatments by Wasielowski resulted in an increasing thickness of the internally oxidized zone with increasing temperature, whereas preoxidation at 800°C eliminated internal oxidation at 1100°C.

The X-ray diffraction data in Table I show that numerous oxides formed during the preoxidation treatment at 800°C but that the Al_2O_3 and NiTiO_3 phases predominated. The intensity of NiO was weak; thus this oxide did not exist as the major phase of the scale. With the exception of one case, inert anneals at either 1000 or 1100°C resulted in the intensification of the reflections from Al_2O_3 . The appearance of $\text{Ni}_2\text{Ti}_4\text{O}$ was also noted (except for the same exception). It thus appears that additional Al_2O_3 formed during the inert anneal, presumably by the reduction of NiTiO_3 by aluminum, the NiTiO_3 being the only source of oxygen. The important aspect to be considered in this reaction is the morphology of the Al_2O_3 film formed during this treatment. If the film were continuous, it would present a barrier to oxygen diffusion and thereby limit internal oxidation during subsequent oxidation at higher temperatures. On the other hand, if the film were not continuous, internal oxidation would occur. Experimentally it was observed that internal oxidation occurred at 1000°C but not at 1100°C. It is therefore possible that either of two processes took place. First, a continuous film existed but subsequently degraded at 1000°C. Second, a noncontinuous film existed which "healed" at 1100°C to form a continuous film, thus preventing internal oxidation. Unfortunately, the extremely thin films formed during the preoxidation were not amenable to metallographic examination, and this point cannot be resolved presently.

The optimum scale to minimize internal oxidation and also to provide maximum overall oxidation resistance is Al_2O_3 . Ionic diffusivities in this oxide are low,^{7,8} although there is little or no knowledge as to what effect doping with the various alloying elements present in IN-1000 would have on the diffusivities (there is little doubt that all of the oxides formed in this system contain most or nearly all of the other elements to some extent). Figure 10 shows a scale that is predominately alumina, the presence of which is associated with good oxidation resistance.

The complexity of the alloy precludes a determination of the critical aluminum concentration required to form a continuous film during low temperature oxidation. If this system is analogous to the silver-indium system on which the classical work on internal oxidation has been performed,⁸ the critical aluminum concentration at a given temperature will increase with increasing oxygen pressure. In other words, low oxygen pressures will be required to enable external oxidation to occur in which case a continuous film would exist. Such a pretreatment might offer more protection than any other treatment or oxidation directly with no pretreatment.

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